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(54) **Air-depolarized button cells**

(57) An air-depolarized button cell, such as a zinc-air cell, is assembled by placing a layer of hydrophobic microporous material 34, preferably polytetrafluoroethylene (PTFE), with a catalytic cathode 22 thereon in a cathode can 12 having an air hole 16 in the bottom thereof. A ring 44 is placed above the cathode electrode, is force fitted within the cathode can, and is pushed downwardly against the cathode electrode structure sufficiently to cause some compression of the PTFE layer 34 beneath the cathode electrode 22 in the area beneath the ring 44. By providing this compressed portion of the PTFE layer, the cathode can is rendered substantially leak-proof, before assembly of the cell.

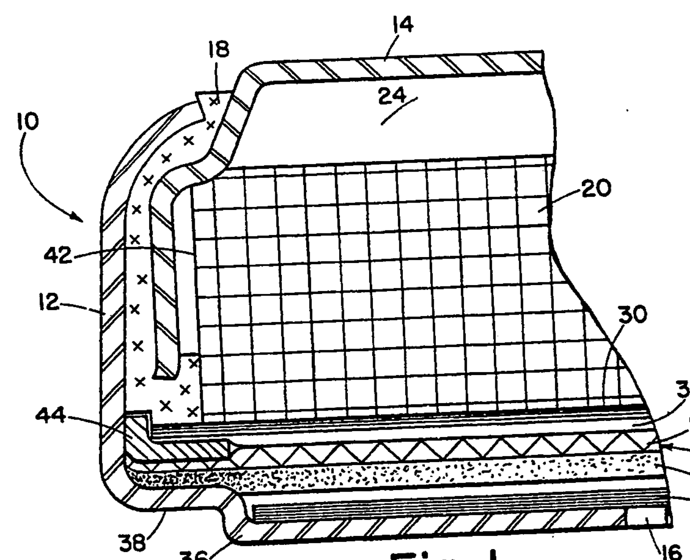

Fig. 1

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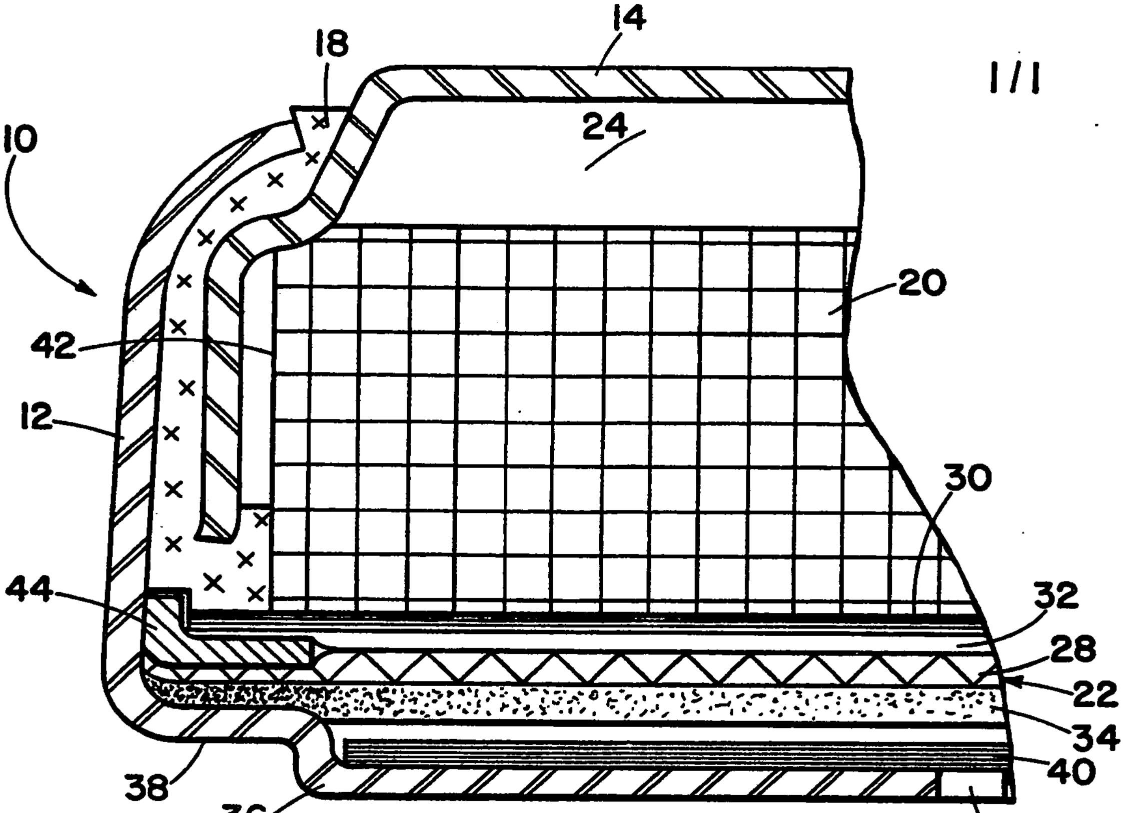

Fig. 1

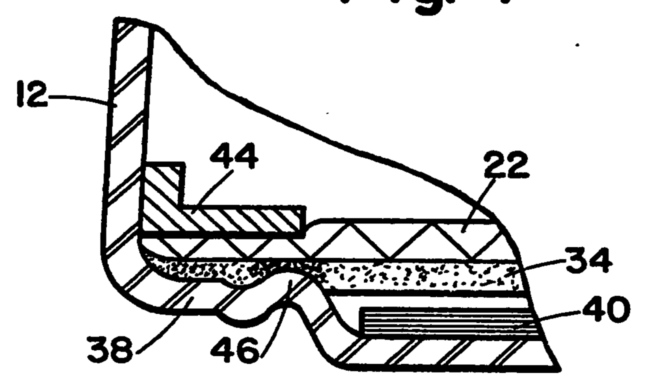

Fig. 2

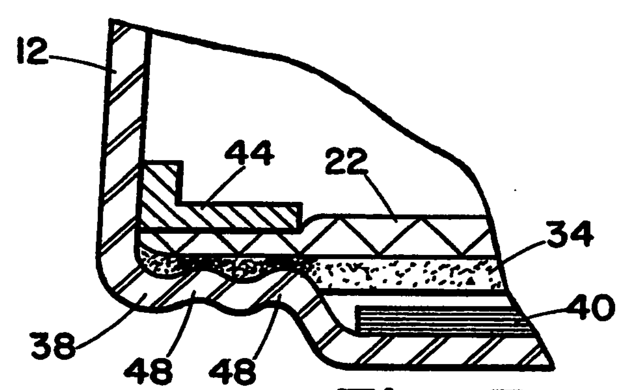

Fig. 3

SPECIFICATION
Air-depolarized button cells

This invention relates to air-depolarized button cells, particularly zinc-air cells. Specifically, this invention relates to the assembly of such cells, including provision for rendering the cathode can of a cell substantially leak-proof prior to final assembly of the cell.

The assembly of zinc-air button cells, on a commercial or mass production basis, of button cells according to the prior art as discussed hereafter, may give rise to significant failure rates of the cells due to faulty or ineffective sealing of the cells and resultant electrolyte leakage. Also, it is desirable to provide zinc-air button cells where contact areas of both the cathode and the anode extend slightly above the periphery of the cell at the respective end thereof.

It is also advantageous, if possible, to utilize standard button cell assembly techniques such as those used for silver or mercury button cells, rather than to develop special methods of handling and equipment specifically for assembly of zinc-air cells—apart from the usual considerations of the materials being handled. In other words, it may sometimes be desirable and advantageous to place the electrode in the cathode can of a button cell, during assembly, at some point prior to assembly of the anode cap into the cathode can and the crimping of them together so as to effect a seal. However, the requisite unsealed nature of such cells (apertures are necessary for air access) frequently causes leakage of the electrolyte from the cathode can, before assembly, by leakage of the electrolyte around the cathode and seepage of the electrolyte toward and out the air access hole or holes in the cathode can.

The prior art has generally not addressed itself to the question of providing a leak-proof seal in the cathode can at such a time that the cathode can is assured to be leak proof prior to assembly of the cell. Generally, total dependence on the crimping action of the cathode can over the anode cap is relied upon for sealing the cell. One approach, however, has been found whereby the seal is accomplished prior to the addition of the electrolyte and cell closure, however the construction is somewhat complicated and requires a special form of cathode can.

Przybyla and Smith, in United States Patent No. 4,066,822 issued January 3, 1978, assigned to a common assignee herewith, have taught in one embodiment of the invention of that patent, a button cell wherein a layer of hydrophobic microporous material is placed in the bottom of the cathode can, and is compressed by forcing down over the hydrophobic microporous material at the periphery thereof a metal ring which has an interference fit within the cathode can, and which, when forced downwardly, compresses the hydrophobic microporous material. At this point, the cathode can has been substantially sealed, prior to the introduction thereinto of any other components.

However, Przybyla et al. also require that the cathode can b such that the central portion of the bottom thereof is recessed upwardly, so that the lowermost portion of the cathode can, and therefore, the principal contact area of the positive terminal for the cell, is at the periphery thereof. Further, a second metal ring is then placed into the cell over the gas depolarizable electrode, to assure electric contact of the electrode to the first ring and thence to the cathode can.

In another patent issued to Przybyla and Smith, U.S. Patent No. 4,118,544, in a similar structure the second ring is removed. However, proper electrical contact is therefore dependent upon pressure from the insulating grommet which is not as desirable.

The Przybyla et al. structures, therefore, require a configuration of elements which reduces the useable volume of the cell, and requires at least one additional element in one embodiment which further reduces the useable volume of the cell or positive electrical contact between cathode and container is dependent upon the resiliency of the insulating grommet which is not desirable Nevertheless, the Przybyla et al. structures assure the leak-proof assembly of the cells, at least to the extent that electrolyte placed within the cathode can will not leak past the cathode and through the air access openings.

Such assurance is not possible in the structure taught by Jaggard in U.S. Patent No. 3,897,265, issued July 1975. That patent specifically requires that the grommet placed between the anode and cathode cups serves the function of an insulator between the metal cups, a sealing member both between the metal cups and as a compression means for compressing the cathode assembly against the cathode cup to inhibit electrolyte leakage out of the air access openings.

However, the sealing of the cathode assembly occurs during the final sealing of the cell and not during intermediary steps during which electrolyte is substantially free to escape from the air access holes. Additionally, the compression from the sealing member merely inhibits electrolyte leakage but does not substantially prevent it. In this respect it is noted that Jaggard provides an electrolyte absorbent member or blotter beyond the "cathode" seal adjacent the air access openings.

Sauer et al., in U.S. Patent No. 4,054,726 issued October 18, 1977 also teach a zinc-air button cell, the principal feature of which is the inclusion within the anode, which is zinc powder, of a compressible expansion body or bodies. Howev r, one feature of the assembly of the Sauer et al. cell is that, not unlike the Jaggard cell, the closing force which occurs when the cathode can is crimped over the grommet and anode cup, causes sufficient force against the edge portion of a hydrophobic layer placed into the cell beneath the air-depolarizabl electrode, and the shoulder

portion of the cathode can at the periphery thereof, so as to preclude electrolyte leakage around the edge of the hydrophobic layer. In the Sauer et al. structure, there is included a ring-like element having an L-shaped configuration, with the vertical leg of the L extending downwardly past the edges of the air-depolarizable cathode electrode and forming part of the electrode structure, for purposes of assuring electrical contact of the cathode structure to the metal cathode can. The sealing of the Sauer et al. structure is, however, as stated above, solely by virtue of the crimping action of the cathode can against the other elements of the cell, during final assembly. Additionally, as in Jaggard, the seal between the cathode assembly and the cathode can is effected only by compression of the resilient sealing member.

In any cell assembly procedure where the electrolyte is placed into the anode cap, assembly of the wetted anode cap into the cathode can may be difficult; and on the other hand, assembly of the cathode can over the anode cap may be difficult, except as the electrode structure within the cathode can is reasonably secured therein.

Accordingly, it may be convenient to follow more conventional button cell assembly procedures and techniques, as practiced in respect of silver and mercury cells, by charging some of the electrolyte into a sealed cathode can, and the remainder of the electrolyte into the anode cap. This is followed by assembly of the cathode can onto the anode cap, which assembly is then crimped. However, because of the air access apertures in the cathode can of air depolarized cells the cathode can is generally not sealed. As a result, electrolyte charging of the cathode frequently causes leakage during cell assembly.

It is an object of the present invention to provide a method of assembly by which electrolyte might be charged into the cathode can, with assurance that the electrolyte will not leak from the cathode can even though there is an air access opening therein.

It is a further object of the present invention to provide an air-depolarized cell structure having improved cathode electrical contact and cathode seal with enhanced volumetric capacity.

The present invention is more fully described hereafter, and its advantages explained, in association with the accompanying drawings, in which:

Figure 1 is a partial cross-section of a typical air-depolarizable button cell, showing the principal components thereof and the application of the present invention thereto;

Figure 2 is a partial cross-section showing an alternative embodiment of the cathode can; and

Figure 3 is a partial cross-section showing yet a furth r embodiment of the cathode can.

Generally, the present invention comprises an assembly of air-depolarized button cells where the cathode can provides a positive terminal for the cell, and an anode cap provides a negative terminal for the cell, with at least one air access opening in the cathode can, and a grommet between the metallic cups to electrically insulate them from each other. Within the cell there is an anode, and an air-depolarizable cathode electric structure, with an electrically insulating and electrolyte absorbing layer between them, and a layer of hydrophobic microporous material beneath the cathode electrode and contacting the bottom of the cathode can. The improvement to the prior art is provided by the addition of a ring element which is placed in the cathode can above the air-depolarizable cathode electrode structure and beneath the electrolyte absorbing separator; where the ring element is force fitted to the cathode can and is pushed against the cathode electrode with sufficient force that the hydrophobic microporous material beneath the cathode electrode is cirumferentially at least partially compressed, at least in part of the area thereof beneath the ring, so as to assure an electrolyte leak-proof structure. Furthermore, at the same time, positive electrical contact is effected between the compressed cathode and the cathode can via the ring element which is in intimate contact with both.

In accordance with the present invention, rapid assembly of the cathode can and the anode cap is not necessary, after the electrolyte has been charged into the cathode can if that procedure is being followed, since there will be no electrolyte leakage around the air-depolarizable cathode structure and the peripheral edges of the hydrophobic microporous layer beneath the electrode structure.

With specific reference to the drawings, Figure 1 depicts an assembly for an air-depolarized button cell 10, where a pair of metallic cups which are intended for nesting one into the other are used. The first is a cathode can 12, which provides the positive terminal for the cell 10, and the second is the anode cap 14, which provides the negative terminal for the cell 10. At least one air access opening 16 is provided in the cathode can 12, so that gas communication from the exterior of the cell 10 to the air-depolarizable electrode structure 22 is assured, as discussed hereafter. The cathode can 12 and anode cap 14 are electrically insulated from each other by a grommet 18; and the grommet provides a seal against electrolyte leakage from the cell 10 outwardly between the walls of the anode cap 14 and the cathode can 12.

Within the cell there is an anode 20 and an air-depolarizable cathode electrode structure 22. A void 24 is shown above the anode 20 and is discussed hereafter.

The air-depolarizable cathode electrode structure 22 comprises a current collector matrix 26 and a catalyzed cathode mix 28 which is intimately associated with the matrix 26. Above the cathode structure 22, and between it and the anode 20, there is an electrolyte absorbing separator layer, which preferably comprises an absorber 30 and a barrier 32.

Beneath the cathode electrode structure 22 is a layer 34 of hydrophobic microporous material. Preferably, that material is polytetrafluoroethylene (PTFE) (or polychlorotrifluoroethylene (PCTFE)), which may be either sintered or unsintered; and preferably the hydrophobic layer 34 is bonded to the cathode structure 22 so as to provide a composite cathode laminate.

The bottom of the cathode can 12 is dished downwardly, at 36, leaving a peripheral shoulder 38. Within the dished portion 36 of the cathode can there is placed a diffusion disc 40 above the air access opening(s) 16.

The anode 20 may be either a pressed pellet (generally comprising zinc amalgam), into which there may also be added a trace of a gelling agent such as carboxymethylcellulose; or the anode 20 may comprise a poured zinc amalgam powder. When the anode is a pressed zinc pellet, it extends to the dotted line 42, and when the anode is a poured zinc powder it will fill the anode cap 14 to the walls thereof. The void 24 is provided within the cell, so as to permit the anode to expand during discharge of the cell.

Above the cathode structure 22, and beneath the barrier 32 and absorber 30, there is provided a ring element or member 44. The ring element 44 provides greater electrical contact between the cathode structure 22 and the cathode can 12 and provides a means of assuring that the cathode can 12 and the elements assembled into it are leak-proof. The ring 44 is force fitted in the cathode can 12; i.e., there is an interference fit between the ring 44 and the interior wall of the cathode can 12, and the ring 44 is pushed or assembled against the cathode structure 22 with sufficient force that the hydrophobic microporous layer 34 beneath the cathode structure 22 is circumferentially at least partially compressed in the area substantially beneath the ring 44. The amount of compression of the hydrophobic microporous layer 34 is generally such that the thickness of the microporous material 34 after the compression is in the order of 30—80% of its initial thickness. By such compression, there is no path provided by which electrolyte placed on the upper surface of the cathode structure 22 can seep past the cathode structure and hydrophobic layer 34 to the area beneath the hydrophobic layer 34. That is, the electrolyte cannot seep past the compressed area of the hydrophobic layer 34. This leak-proof seal is assured by virtue of the force fit of the ring 44 within the cathode can 12, so that once placed it will not move out of place.

Preferably, the ring element 44 has an L-shaped cross-section, with the vertical leg of the L extending away from the electrode structure 22, and the horizontal leg of the L extending inwardly from the wall of the cathode can 12 across the upper surfac of the cathode structure 22.

In the preferred embodiment, the horizontal leg of the L-shaped cross section of ring 44 is longer than the vertical leg. This is not limiting, however, and other cross-sections such as straight, triangular or circular may be possible, providing that there is an interference fit between the outer diameter of the ring 44 and the inner diameter of the cathode can 12. Obviously, the L-shaped configuration provides the stiffest ring for the volume taken up by it.

It will also be noted that, when the ring element 44 is pushed against the cathode structure 22 there is some compression of the cathode structure 22 in the area beneath the ring 44 to ensure positive electrical contact therewith and there is forced transmission through the cathode structure 44 to cause compression of the hydrophobic layer 34. The compression of the hydrophobic layer 34 may be aided by the provision of the shoulder portion 38, above the dished portion 36 of the bottom of the cathode can 12. Several alternative embodiments of the shoulder portion of the cathode can 12 are shown in Figures 2 and 3, whereby a ridge 46 is formed in the shoulder portion 38 of the cathode can 12 as shown in Figure 2, or a pair of concentric ridges 48 is formed in the shoulder portion 38 as shown in Figure 3.

In order to assure the interference fit of the ring 44 into the cathode can 12, normally it is formed so that its outside diameter is, before assembly into the cathode can, slightly greater than the inside diameter of the cathode can.

The purpose of the diffusion disc 40, in the bottom of the cathode can 12, is to assure that air entering the can through the air access opening 16 is diffused across the bottom of the composite cathode/hydrophobic layer laminate, to thereby assure air access to the working area of the cathode. Likewise, the placement of the anode 20 above the cathode structure 22 ensures that the anode fully faces the cathode, when the cell is operating.

By adopting the ring element 44 as used in the assembly of silver oxide cells for generally different purposes, conventional button cell assembly techniques and methods can be used in making the air depolarized cells of the present invention. In particular, the necessity for special tools, sizing dies, and the like is precluded, and there is no special handling technique for assembling the anode cap into the cathode can, so as to preclude electrolyte leakage. Further, during assembly of cells according to this invention, there is no chance for electrolyte to be forced; i.e., pumped, past the hydrophobic layer in the bottom of the cathode can and out the air access hole.

By this invention, there has been eliminated the requirement for reliance upon the sealing pressure of the sealing grommet so as to preclude leakage of electrolyte past the cathode structure to the air access openings of the cell. Still further, additional rings for ensuring positive electrical contact or other structure have been substantially eliminated, so that the interior volume of the cell can be dedicated to active materials, thereby increasing the capacity of the cell.

A specific example follows, showing utilization

of the present invention in the assembly of a zinc-air cell.

Exampl

A number of zinc-air button cells each having 0.455 inches (1.16 cm) O.D. and 0.210 inches (0.53 cm) height, are assembled, in which the cathode can is formed of nickel-plated steel having straight walls before assembly with an inside diameter of 0.434 inches (1.10 cm). The anode cap is a standard triclad material (copper/steel/nickel), with a maximum diameter of 0.405 inches (1.03 cm). A nylon grommet is placed between the cathode can and anode cap. A bonded cathode/PTFE structure is placed in the cathode can, over a diffusion disc of filter paper, with the thickness of the bonded cathode laminate being 0.022 inches (0.056 cm). The total thickness of the barrier and absorber layers is 0.005 to 0.008 inches (0.013 to 0.020 cm). The ring element is formed of pure nickel with an outer diameter of 0.436 inches (1.11 cm) before assembly into the cathode can; and an inner diameter between the inner edges of the horizontal extending legs of 0.340 inches (0.86 cm). It will be noted that the external diameter of the ring exceeds the internal diameter of the cathode can by approximately 0.002 inches (about 0.005 cm).

The anode is comprised of a compressed pellet of amalgamated zinc powder, and the electrolyte is a potassium hydroxide (KOH) solution.

The hydrophobic membrane is unsintered PTFE, with a thickness of 0.010 inches (0.025 cm). Upon assembly into the cell, the thickness of the PTFE layer is reduced by approximately 50% in the area beneath the ring and above the shoulder of the cathode can. All of the cells assembled, according to the above, demonstrate excellent operating characteristics, and do not leak during assembly, storage or operation.

It should be noted that the ring element might conveniently be nickel, or nickel plated steel, or other suitable material. It is noted that the present invention is particularly adaptable to and intended for use in air-depolarized button cells, and particularly as set forth in the appended claims.

Claims

1. An air-depolarized cell assembly, comprising a pair of cups nesting one into the other, the first being a cathode can providing a positive terminal for the cell, and the second being an anode cap providing a negative terminal for the cell; at least one air access opening in said cathode can providing gas communication from the exterior to the interior of said cell; a grommet between said cups for electrically insulating them; an anode, an air-depolarizable cathode electrode structure, an electrolyte absorbing separator layer between them, and a layer of hydrophobic microporous material between said cathode electrode and the inner base surface of said cathod cup and in contact with the said surface; a ring element in place in said cathode can between said air-depolarizabl cathode electrode and said electrolyte absorbing separator layer, said ring element being in force-fit engagement against said cathode electrode so that said hydrophobic microporous material beneath said cathode electrode is circumferentially, at least partially compressed in the area beneath said ring.

2. The assembly of claim 1, wherein said ring element has a substantially L-shaped cross-section; where the vertical leg of said L extends away from said cathode electrode, and the horizontal leg of said L extends inwardly away from the wall of said cathode can.

3. The assembly of claim 1 or 2, wherein the outside diameter of said ring member, before assembly into said cell, is sligthly greater than the inside diameter of said cathode can.

4. The assembly of claim 1, 2 or 3, wherein the bottom of said cathode can has at least one ridge formed therein near the periphery thereof.

5. The assembly of any preceding claim wherein the thickness of said hydrophobic microporous material, after said ring member is put into place, is 30—80% of its initial thickness.

6. The assembly of any preceding claim wherein said electrolyte absorbing separator layer comprises a barrier layer and an absorber layer.

7. The assembly of any preceding claim, further comprising a porous diffusion disc placed in said cathode can beneath said hydrophobic microporous material.

8. The assembly of claim 7, where the bottom of said cathode can if dished downwardly, and said diffusion disc is disposed in said dished portion.

9. The assembly of any preceding claim, wherein said air-depolarizable cathode electrode and said hydrophobic microporous material are bonded together.

10. The assembly of any preceding claim, wherein said hydrophobic microporous material is chosen from the group consisting of sintered polytetrafluoroethylene and unsintered polytetrafluoroethylene.

11. A method of constructing an air-depolarized cell comprising a cathode cup with at least one aperture therein and a nesting anode cup, wherein a layer of a hydrophobic microporous material is placed within said cathode cup contacting the bottom thereof and wherein layers of and air-depolarizable cathode electrode structure and an electrolyte absorbing separator are sequentially placed thereafter into said cathode cup, said cathode cup is thereafter filled with electrolyte prior to nesting of said anode cup and an anode active material into said cathode cup and sealing of said cell, characterized in that said method comprises, prior to said filling with electrolyte, the step of placing a ring element in said cathode can above said air-depolarizable cathode electrode and beneath said electrolyte absorbing separator layer into force fitting engagement against said cathode electrode such that said hydrophobic microporous material is

circumferentially, at least partially compressed in the area beneath said ring whereby leakage from said cathode cup during the subsequent addition of electrolyte is prevented.

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